ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 5, pp. 1007–1008. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © T.S. Khlebnikova, V.G. Isakova, F.A. Lakhvich, 2008, published in Zhurnal Obshchei Khimii, 2008, Vol. 78, No. 5, pp. 864–865.

LETTERS
TO THE EDITOR

Reduction of 2-Perfluoroalkanoylcyclohexan-1,3-diones Under the Conditions of Ionic Hydrogenation

T. S. Khlebnikova, V. G. Isakova, and F. A. Lakhvich

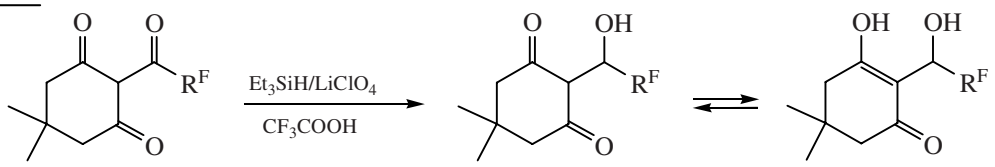
Institute of Bioorganic Chemistry, Belarus National Academy of Sciences,
ul. Akad. Kuprevicha 5/2, Minsk, 220141 Belarus
e-mail: khlebnicova@boch.bas-net.by

Received December 20, 2007

DOI: 10.1134/S1070363208050290

2-Perfluoroalkanoylcyclohexan-1,3-diones we described recently [1,2] present significant interest as the promising building blocks for introducing polyfluoroalkyl groups in various carbo- and hetero-cyclic systems. Unlike nonfluorinated cyclic β,β'-triketones [3] the chemistry of these compounds is studied unsufficiently, and investigation of their chemical transformations, in particular, in reduction, is an important problem for the chemistry and the synthetic use of these polyfunctional compounds. The ionic hydrogenation of nonfluorinated 2-cycloalkan-1,3-diones is known to proceed regioselectively with the prevailing hydrogenolysis of the keto group in the side chain to give the methylene group and resulting in the formation of 2-alkylcycloalkan-1,3-diones [4]; this has been successfully used for the synthesis of prostaglandines [5] and phytoprostanes [6].

The aim of this work is the investigation of the behavior of 2-perfluorocyclohexan-1,3-diones **Ia, Ib** under the conditions of ionic hydrogenation. It was found that the ionic hydrogenation of 2-trifluoroacetyl- **Ia** and 2-pentafluoropropyonyl dimedone **IIa** with triethylsilane in trifluoroacetic acid in the presence of lithium perchlorate within 5 h at room temperature resulted in the reduction of exocyclic carbonyl group to hydroxy one to afford diketoalcohols **IIa, IIb** in 81% and 89% yield respectively. At the increased reaction time (24 h and more) only compounds **IIa, IIb** were isolated.



Ia, Ib **IIa, IIb**

R^F = CF_3 (**a**), C_2F_5 (**b**).

Hence, unlike the nonfluorinated cyclic β,β'-triketones the reduction of 2-perfluoroacylcyclohexan-1,3-diones **Ia, Ib** under the conditions of ionic hydrogenation leads to selective formation of diketoalcohols **IIa, IIb** that can be ascribed to the effect of the electron-accepting perfluoroalkyl substituent.

We used the ionic hydrogenation for the reduction of the other polyfluorinated 2-acylcyclohexan-1,3-diones and their derivatives. The results will be described in further publications.

The structure of diketoalcohols synthesized **IIa, IIb** existing in the enol form was confirmed by IR and ^1H, ^{13}C, and ^{19}F NMR spectroscopy and the elemental analysis.

The starting compounds **Ia, Ib** were prepared according to procedure [1, 2].

2-(1-Hydroxy-2,2,2-trifluoroethyl)-5,5-dimethylcyclohexan-1,3-dione (IIa). To a solution of 1 mmol of compound **Ia** in 2 ml of trifluoroacetic acid 2 ml of 1% lithium perchlorate solution in trifluoroacetic acid and 4 mmol of triethylsilane were added. The reaction mixture was stirred at room temperature for 5 h. Trifluoroacetic acid was distilled in a vacuum, the residue was washed with small amount of *n*-hexane (4 × 4 ml) and crystallized from the acetone–hexane mixture. Yield 81%, mp 83–86°C. The IR spectrum, ν, cm^{-1}: 1615 (C=O conjugated), 155 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.08 (6H, $2CH_3$), 2.31 d (2H, CH_2, *J* 17.1 Hz), 2.36 d (2H, CH_2, *J* 17.1 Hz), 5.40 m (1H, C*H*OH). ^{13}C NMR spectrum (Py-d_5), δ_C, ppm: 27.98, 31.93, 47.93, 67.38 q ($^3J_{CF}$ 32 Hz), 105.87, 126.07 q ($^1J_{CF}$ 285 Hz), 190.42. ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: −76.68 d (J_{FH} 7 Hz). Found, %: C 50.51, H 5.56. $C_{10}H_{13}F_3O_3$. Calculated, %: C 50.42, H 5.50.

2-(1-Hydroxy-2,2,3,3,3-pentafluoropropyl)-5,5-dimethylcyclohexan-1,3-dione (IIb) was obtained analogously from the compound **Ib**. Yield 89%, mp 90–93°C. IR spectrum, ν, cm^{-1}: 1610 (C=O conjugated), 1555 (C=C). ^1H NMR spectrum ^1H ($CDCl_3$), δ, ppm: 1.09 s (6H, $2CH_3$), 2.32 d (2H, CH_2, *J* 17.1 Hz), 2.36 d (2H, CH_2, *J* 17.1 Hz), 5.53 d.d (1H, C*H*–OH, *J* 18.0, 7.6 Hz). ^{13}C NMR spectrum (Py-d_5), δ_C, ppm: 28.04, 31.94, 47.78, 66.81 d.d ($^2J_{CF}$ 28, 23 Hz), 105.59, 115.62 t.q ($^1J_{CF}$ 258, $^2J_{CF}$ 34 Hz), 120.46 q.t ($^1J_{CF}$ 287, $^2J_{CF}$ 36 Hz), 190.05. ^{19}F NMR spectrum (Py-d_5), δ_F, ppm: −81.53 s (3F, CF_3), −121.29 d.d (1F, J_{FF} 270, J_{FH} 6 Hz), −128.30 d.d (1F, J_{FF} 269, J_{FH} 22 Hz). Found, %: C 45.92, H 4.61. $C_{11}H_{13}F_5O_3$. Calculated, %: C 45.84, H 4.55.

NMR spectra were taken on a Bruker Avance-500 spectrometer, internal reference TMS for ^1H (500 MHz) and ^{13}C (125 MHz), and CCl_3F, for ^{19}F (470 MHz. IR spectra were recorded on an UR-20 spectrometer from KBr pellets. Melting points were measured in a Boetius block. The reaction progress and the purity of the compounds obtained were monitored by TLC on Silufol UV-254 plates, eluent ether.

REFERENCES

1. Khlebnicovaб T.S., Zinovichб V.G., and Lakhvich, F.A., *Dokl. Nat. Acad. Nauk Belarus*, 2005, vol. 49, no. 5, p. 72.
2. Khlebnicova, T.S., Isakova, V.G., Baranovsky, A.V., Borisov, E.V., and Lakhvich, F.A., *J. Fluorine Chem.*, 2006, vol. 127, no. 12, p. 1564.
3. Rubinov, D.V., Rubinova, I.L., and Akhrem, A.A., *Chem. Rev.,* 1999, vol. 99, no. 4, p. 1047.
4. Akhrem, A.A., Lakhvich, F.A., Lis, L.G., Khripach, V.A., Fil'chenkov, N.A., Kozinets, V.A., and Pashkovskii, F.S., *Dokl. Akad. Nauk SSSR*, 1990, vol, 311, no. 6, p. 1381.
5. Lakhvich, F.A. and Kozinets, V.A., *Zh. Org. Khim.*, 1997, vol. 33, no. 1, p.53.
6. Schmidt, A. and Boland, W., *J. Org. Chem.*, 2007, vol. 72, no. 6, p. 1699.